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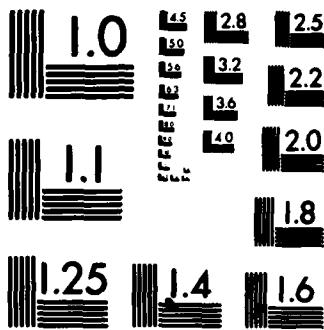
ELECTRONIC STRUCTURE OF LANGMUIR-BLODGETT FILMS ON BARS 1/1
AND OTHER MATERIALS(U) UNIVERSITY OF STRATHCLYDE
GLASGOW (SCOTLAND) DEPT OF PHYSICS B HENDERSON

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ELECTRONIC STRUCTURE OF LANGMUIR-BLODGETT

FILMS ON GaAs AND OTHER MATERIALS

By

PROFESSOR B. HENDERSON

Department of Physics,
University of Strathclyde,
John Anderson Building,
107 Rottenrow,
Glasgow, G4 0NG,
Scotland.

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1. Scientific Programme

The intent of this preliminary programme was to deposit Langmuir-Blodgett (LB) films on semiconductor surfaces, and assess their structure, thickness and perfection using a variety of experimental techniques. In doing this we have contributed to rehousing Professor Pethrick's L-B trough in a 'clean room' in the Chemistry Laboratory. This followed advice from Dr. M. Petty at Durham University, largely because we have experienced difficulties in obtaining reproducible results with many samples. To date our work has been concerned with GaAs, GaP and Si, all in the form of (111) wafers, which had been mechanically polished to an $0.25\mu\text{m}$ finish using diamond paste, prior to chemical polishing and refluxing for several hours in isopropyl alcohol vapour. Such samples were assumed to be clean, and were kept in an evacuated chamber until ready to be treated in the L-B trough.

The L-B films that we have used include Cu-phthalocyanine (CPT), metal-free phthalocyanine (MFPT) and 12-8 substituted diacetylene (12-8 SDA). Given due care very clean, defect free interfaces can be prepared between semiconductor and organic insulator, and films varying in thickness from a monolayer up to several hundred layers have been prepared, deposited monolayer at a time. The technique developed was to dissolve the organic compound in a suitable solvent, (e.g. chloroform worked very well with each of the above compounds), and then spread this solution on the surface of pure water obtained from a Millipored water purification system. Once the solvent has evaporated, individual molecules are left floating on the surface. Semiconductor wafers are then dipped into the trough in a controlled

manner. For success the molecules to be deposited must have carefully balanced hydrophilic and hydrophobic regions if the initial monolayer and subsequent multilayers are to be formed. By compressing the surface area molecules are made to form a quasi-layer one molecule thick. An electronic feedback system maintains the surface pressure constant at programmed desorption measurements, and surface enhanced second harmonic generation.

2. Optical Absorption Studies

Measurements in the visible spectrum of L-B films composed of Cu-phthalocyanine (CPT) showed that after ca 15 monolayers a recognisable broad absorption band with peak at 614nm due to the $^2E \rightarrow ^2T$ transition of the Cu $^{2+}$ ion was discernable. The absorbance of the sample, which from de Beer's law is

$$\frac{\Delta I}{I_0} = 1 - \exp - \alpha(\nu) \ell \approx \alpha(\nu) \ell$$

for thin samples, grew linearly with the number of layers as is shown in Fig.1 for GaP. This behaviour was independent of the semiconductor substrate; measurements being taken in reflection at an angle of 15°.

Thin films of 12-8 diacetylene monomer were immediately polymerized by exposure to an intense ultra-violet lamps for up to 2 hours at room temperature. Measurements of the optical absorption coefficient in the range between $0.5-3.0 \times 10^{-2} \text{Nm}^{-1}$. A programmable control unit sets the number of layers to be coated and controls the speed of dipping. With a hydrophilic substrate (Si, GaAs, GaP) no film is deposited during the first immersion; the first monolayer is

deposited during the first withdrawal. Thereafter one monolayer coverage is obtained for each traversal of the water surface. In this way multilayer structures can be built up to about $1\mu\text{m}$ thickness.

We have deposited thin (5 layers) and thick (100 layers) of each organic material on each of the three semiconductors. The films were then studied using visible and infra-red optical absorption, electron spin resonance (ESR), low energy electron diffraction (LEED), temperature - 300nm to $14\mu\text{m}$ showed optical absorption with peak at 485nm giving the polymerized L-B films a distinct reddish hue. Again this band did not appear until some 20-25 monolayers had been deposited, and thence the absorptivity ($\Delta I/I$) increased linearly with the number of layers. A similar behaviour was observed for two weak infra-red absorption bands at frequencies of 2936cm^{-1} (asymmetric stretch) and 2860cm^{-2} (symmetric stretch), both being due to vibrational modes of the CH_2 group.

3. Electron Spin Resonance Studies

As reported in the preliminary report ESR spectra of Cu^+ ions in CPT were quite distinct showing the essential ingredients of an $S=\frac{1}{2}$ electronic system with attendant superhyperfine structure due to four nearest neighbour N-nuclei ($I=\frac{1}{2}$). The appropriate spin Hamiltonian takes the form

$$H = \mu_B B \cdot g \cdot \underline{S} + \sum_I I \cdot A \cdot \underline{S}$$

and the spectra are typical of bulk single crystal CPT. Again the spin concentration increased monotonically with increasing numbers of monolayers.

No resonances were discernible in semiconductor wafers with M-FPT or 12-8 SDA monomer. This is hardly surprising since none of the samples (GaAs, GaP or Si) showed surface defect ESR prior to dipping in the L-B trough. However after polymerization to form 12-8 SDAP a weak free electron resonance ($g \sim 2.00$) was observed, presumably due to dangling bond formation on a small number of C-bonds. We also carried out a number of experiments with Si/SiO₂ wafers, on which the SiO₂ (thermally grown) was of thickness up to 100nm. Such samples were first γ -irradiated to maximise the concentration of P_b centres. Growth of SiO₂ on Si substrates can, if due care is not taken, result in the presence of 'pin-holes' through the oxide. It then becomes impossible to apply significant gate voltages across the Si/SiO₂ interface. With good oxide films it is possible to study the strength of the P_b centre signal as a function of gate voltage. However, even 'leaky' films once given L-B coating of organic insulator sustains large gate voltages. Our measurements show that the P_b centre saturates at large negative gate voltages, due to spin-spin interactions between P_b centres and charge carriers at the interface. However as the applied gate voltage becomes steadily less negative the P_b centre spin-spin relaxation time becomes shorter and is no longer saturated (Figure 2). This latter result applies for even bad SiO₂ films, once the L-B film had been attached. The M-FPTC and 12-8 SDAP are much better than CPTC in this respect.

4. Low Energy Electron Diffraction

This technique offers a convenient method of studying surface crystallography, although there is a certain technical difficulty due

to the fact that ultra-high vacuum (UHV) is required. This study showed that no surface charging due to electron beam processing takes place, and that no damage of the L-B film takes place at either the monolayer or multi-layer level. However, the monolayer structure of CuPTC and MFPTC is of a different structure from any bulk PTC plane and that subsequent growth depends upon the first monolayer structure. However, the PTC films are always polycrystalline, although the LEED pattern shows that highly ordered layers are formed, as they must in view of the very simple ESR spectrum.

5. Temperature Programmable Desorption

This is another UHV technique, in which the sample is heated in a controlled manner, and the desorption of the film from the semiconductor sample is monitored using a mass spectrometer. Since the mass spectrometer system has a limit of 250 a.m.u. the technique to be operational would require there to be 'cracking' of the molecular unit. In CPTC molecular fragments were observed to appear near 190°C with masses of ca 60 a.m.u. (Cu), 20 a.m.u. (NH_4) and 14 a.m.u. (CH_2). In 12-8 SDAP the temperature at which desorption was first observed was ca 270°C. However these were preliminary results and much greater accuracy and control is necessary to enable measurements to be made of the adhesive strength.

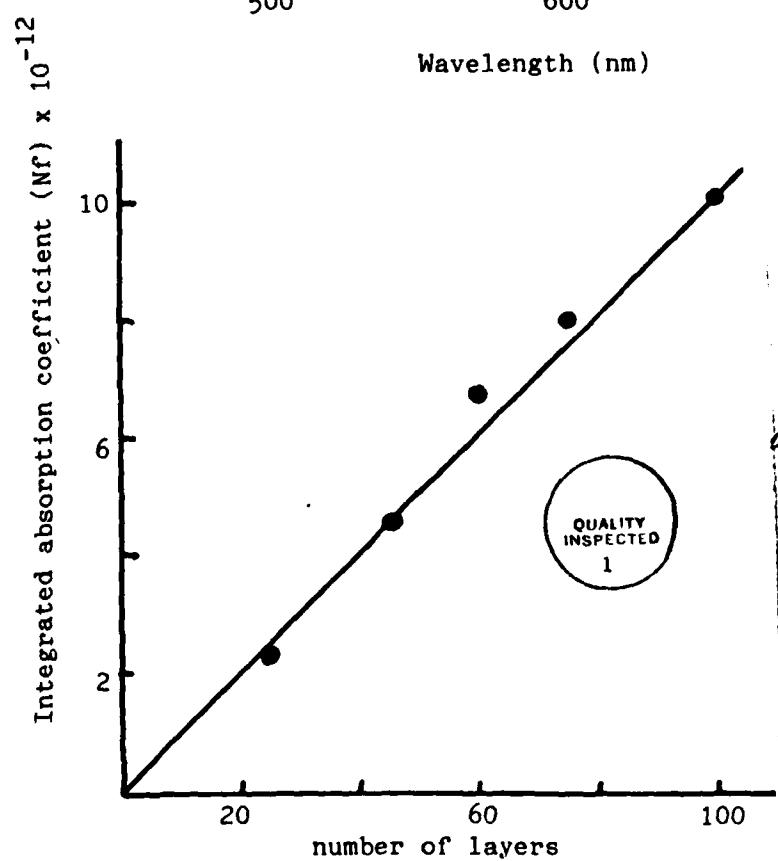
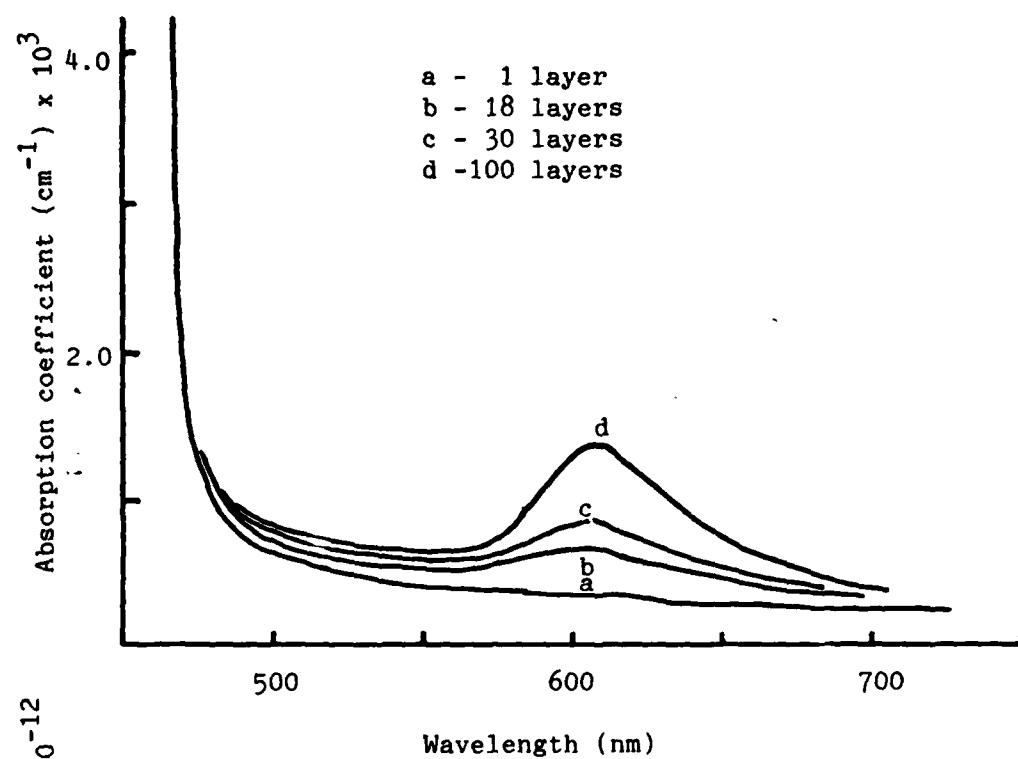
6. Surface Enhanced Second Harmonic Generation

Here we rely upon second order non-linear optic coefficient enabling a laser beam at frequency ν to be converted to radiation at frequency 2ν . The sample is once more held in an UHV chamber, and

pulsed laser radiation at $1.06\mu\text{m}$ directed normal to the surface. Radiation at 532nm is measured normal to the surface through an interference filter which passes this wavelength. In centro-symmetric crystals such as Si, GaAs and GaP the coefficient $X_2 = 0$ for bulk materials. However dipolar interactions at the surface result in $X_2 \gg 0$ for the surface layer, because the centre of symmetry no longer exists. There is then a strong second harmonic signal, as we have observed for Si, GaAs and GaP. However if a small partial pressure of O_2 is allowed onto the Si, which is heated to ca 500°C , this signal dies over a period of 15 minutes (Fig.3). This is due to the growth of SiO_{2-x} on the surface. The decay of this signal with time is much slower for GaAs and GaP. However if the Si/ SiO_2 samples are coated with a 12-8 SDAP L-B film an enormous second harmonic signal is produced the strength of which is linear in the number of monolayers (Fig.4).

7. Concluding Remarks

This has been a preliminary study of the properties of L-B films, which indicates that optical techniques and ESR can play a useful role in characterizing the films. However TPD shows that some films, although strongly adhesive at room temperature, rapidly desorb at temperatures above 250°C , so that they are unlikely candidates for passivating layers on device materials, at least when present in an hostile environment. Such materials are an interesting adjunct to the evergrowing list of non-linear optic materials for harmonic generation of laser light.



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Figure 1 Showing (a) optical absorption coefficient of CuPTC L-B Films on GaP and (b) integrated absorption coefficient (effectively $Nf \times$ oscillator strength f) under 614 nm band versus number of monolayers.

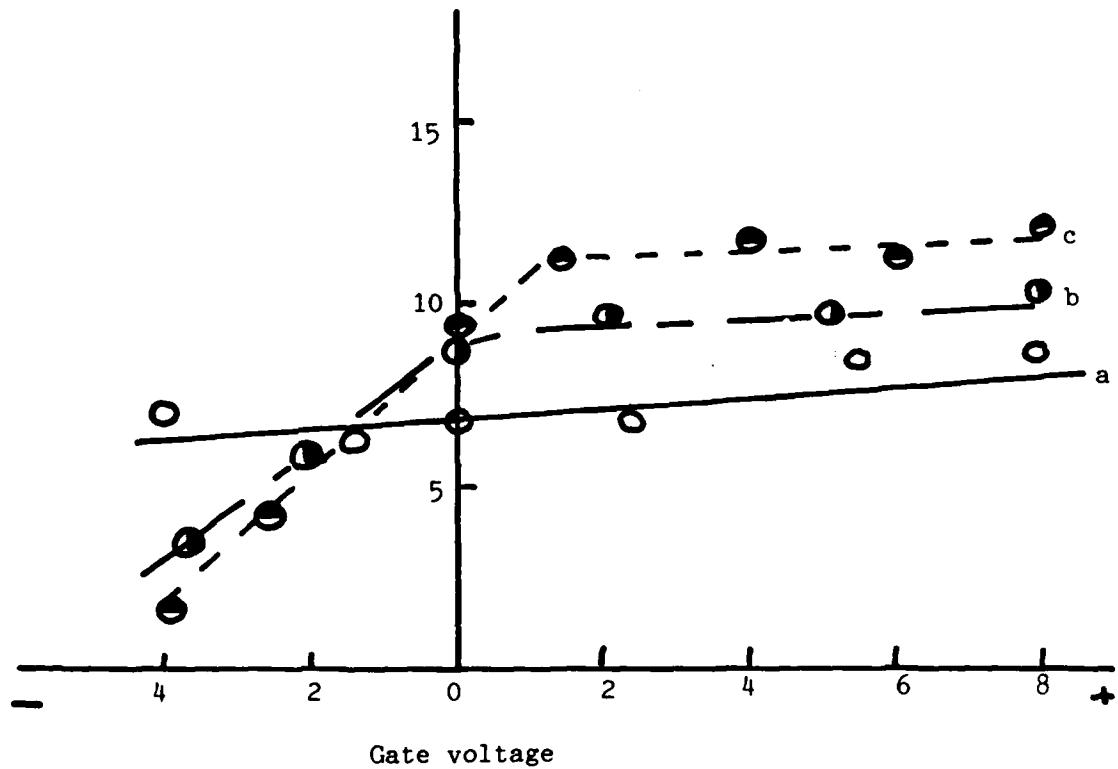


Figure 2 Showing the variation in ESR signal of P_b centres with gate voltage for a) Si/SiO_2 wafer with 'poor' oxide film
 b) Si/SiO_2 wafer with carefully prepared film c) Si/SiO_2 wafer (SiO_2 layer of thickness 10nm) with 10 layers of polymerized 12-8 SDAP.

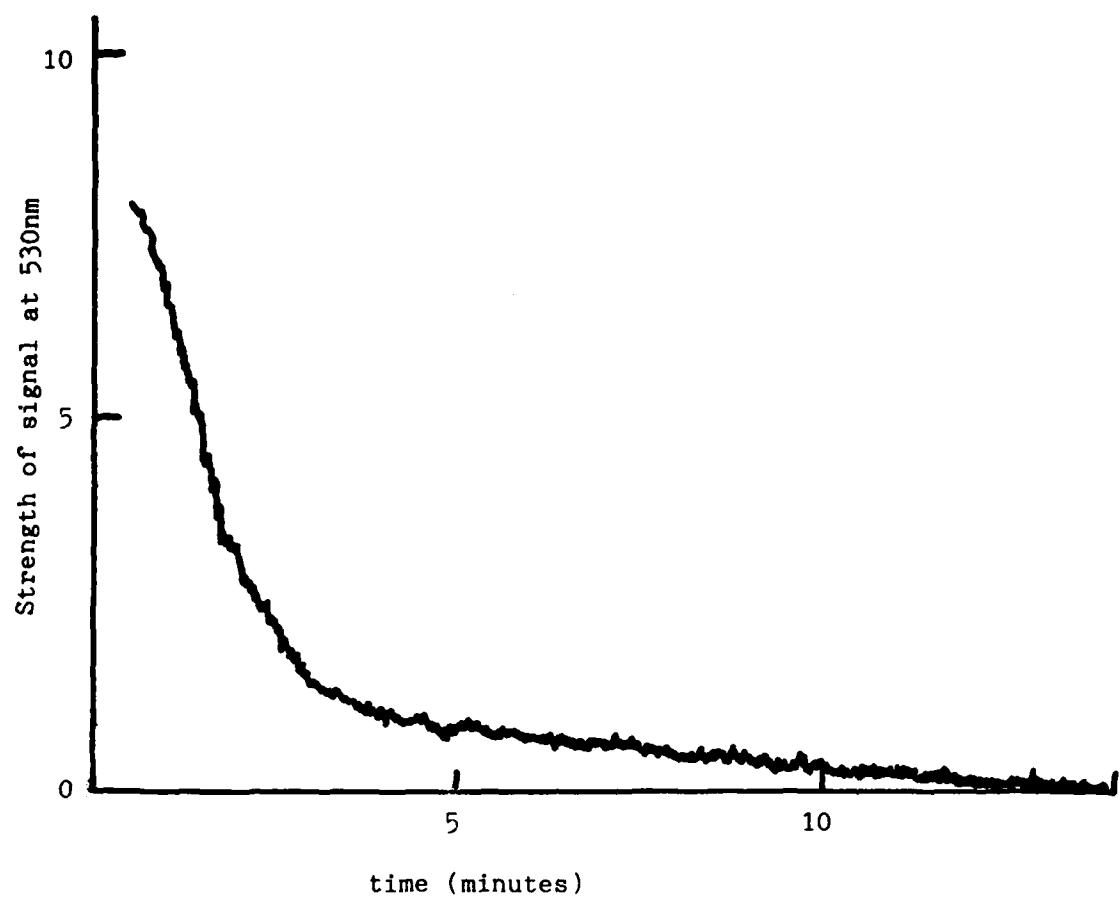


Figure 3 Showing the decrease in intensity of the second harmonic signal at a 'clean' Si surface during oxidation.

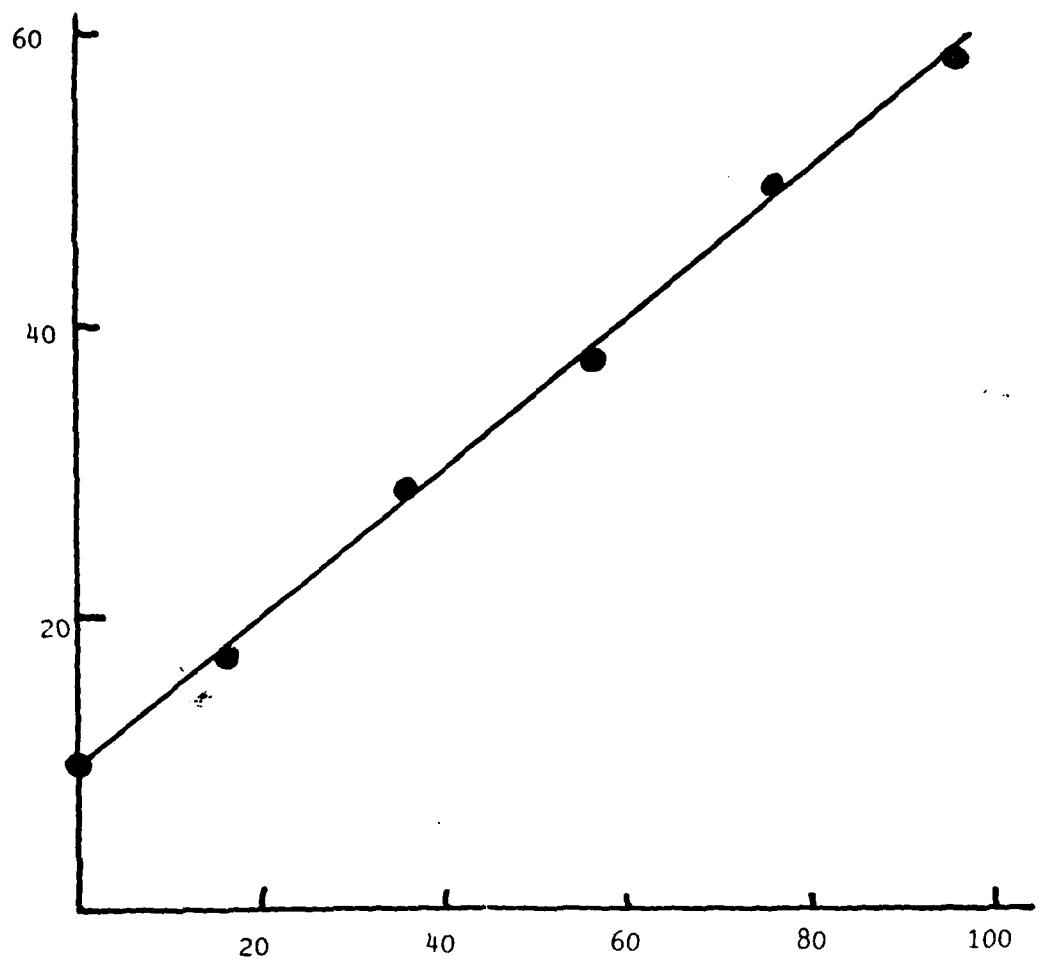


Figure 4 Showing enhancement of second harmonic signal by 12-8 SDAP monomer monolayers.

INVOICE

DATE 30 January 1986

NAME OF CONTRACTOR Professor B. Henderson

CONTRACT NUMBER DAJA 45-84-C-0047

ADDRESS OF CONTRACTOR Department of Physics
University of Strathclyde
John Anderson Building
Glasgow G4 0NG
Scotland

041 552 4400 Extn.3255

ITEM 1 Preparation and submission of 3rd Interim
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